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(54) **COBALT-BASE ALLOY WITH HIGH HEAT RESISTANCE AND HIGH STRENGTH AND PROCESS FOR PRODUCING THE SAME**

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(58) **Field of Classification Search**

CPC C22C 19/07; C22F 1/10

USPC 148/674

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,960,552 A 6/1976 Woulds
4,082,548 A 4/1978 Kleemann et al.

(Continued)

FOREIGN PATENT DOCUMENTS

JP 59-129746 A 7/1984
JP 10-102175 A 4/1998
JP 2004-238720 A 8/2004

OTHER PUBLICATIONS

NPL: translation of JP2004238720, Aug. 2004.*

(Continued)

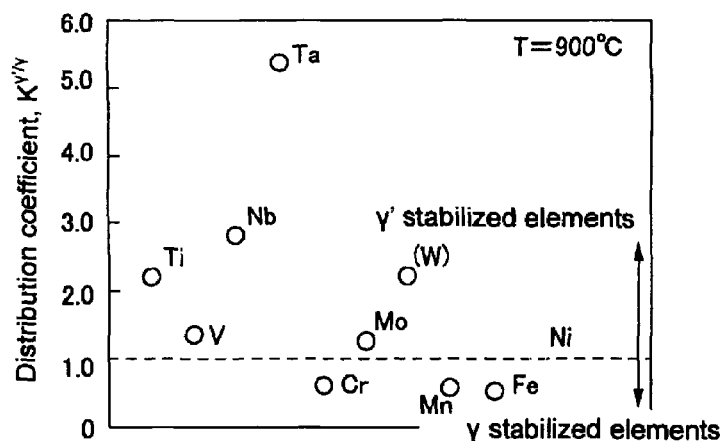
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(57) **ABSTRACT**

A process for producing a Co-base alloy which has a basic composition including, in terms of mass proportion, 0.1%-10% Al, 3.0-45% W, and Co as the remainder and has an intermetallic compound of the L1₂ type [Co₃(Al,W)] dispersed and precipitated therein. Part of the Co may be replaced with Ni, Ir, Fe, Cr, Re, or Ru, while part of the Al and W may be replaced with Ni, Ti, Nb, Zr, V, Ta or Hf. The intermetallic compound [Co₃(Al, W)] has a high melting point, and this compound and the matrix are mismatched little with respect to lattice constant. Thus, the cobalt-base alloy can have high-temperature strength equal to that of nickel-base alloys and excellent structure stability.

18 Claims, 12 Drawing Sheets



(56)

References Cited

U.S. PATENT DOCUMENTS

4,152,181	A	5/1979	Hirakis
4,606,887	A	8/1986	Hausselet et al.
4,765,955	A	8/1988	Yabuki et al.
2008/0185075	A1	8/2008	Ishida et al.
2008/0206090	A1	8/2008	Ishida et al.

OTHER PUBLICATIONS

H. Chinen et al., "New ternary compound Co₃(Ge,W) with L12 structure.", Scripta Materialia, vol. 56, (2007), pp. 141-143.
 D.H. Ping et al., "Microstructure of a newly developed g' strengthened Co-base superalloy.", Ultramicroscopy, vol. 107, (2007), pp. 791-795.

J. Sato et al., "Cobalt-base high-temperature alloys.", Science, vol. 312, (2006), pp. 90-93.

A. Suzuki et al., "Flow stress anomalies in g/g' two-phase Co-Al-W-base alloys.", Scripta Materialia, vol. 56, (2007), pp. 385-388.

Q. Yao et al., "Structural stability and elastic property of the L12 ordered Co₃(Al,W) precipitate." Applied Physics Letters, vol. 89, (2006), pp. 161906-(1-3).

C. Jiang, "First principles study of Co₃(Al,W) alloys using special quasi-random structures." Scripta Materialia, vol. 59, (2008), pp. 1075-1078.

International Search Report of PCT/JP2006/317939, mailing date of Oct. 17, 2006.

* cited by examiner

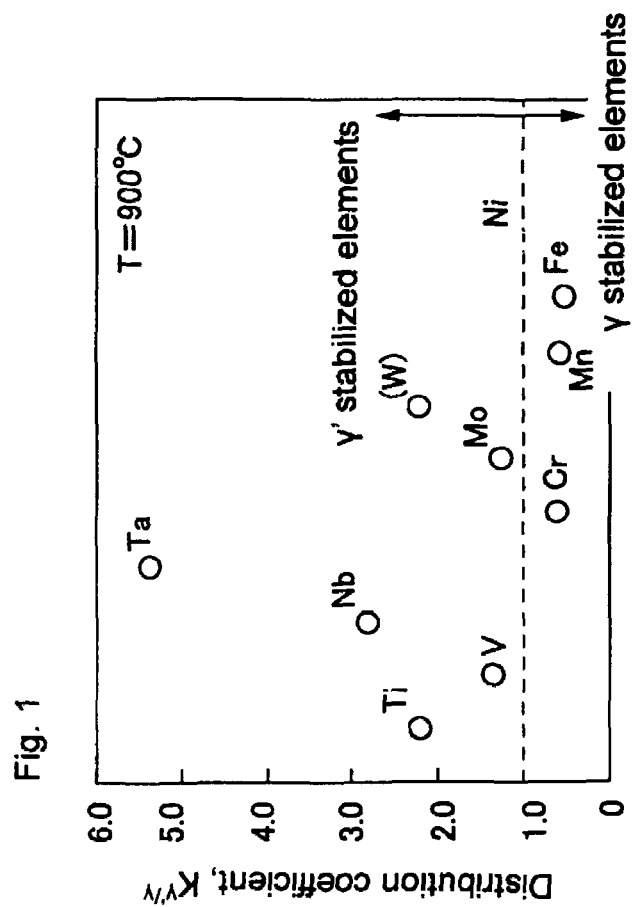


Fig. 2

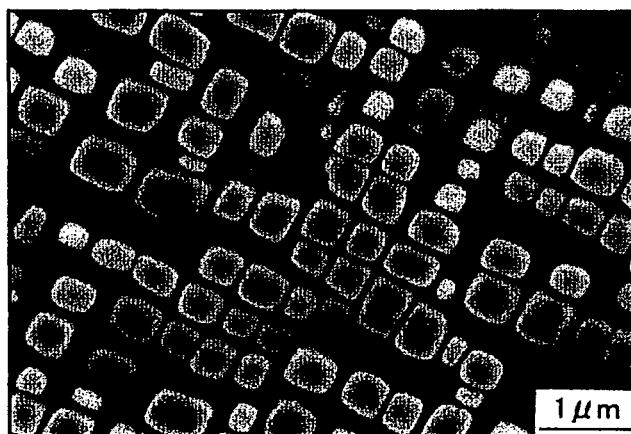


Fig. 3

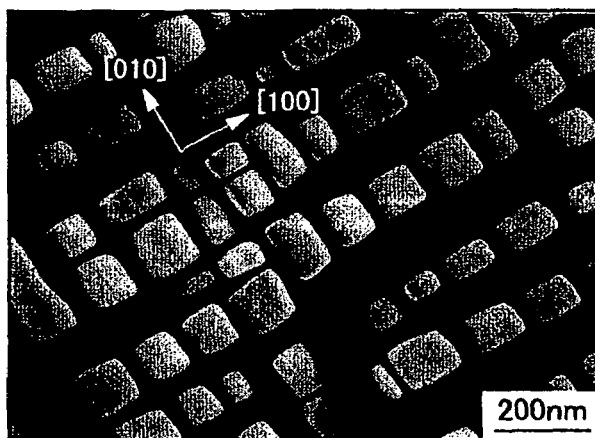
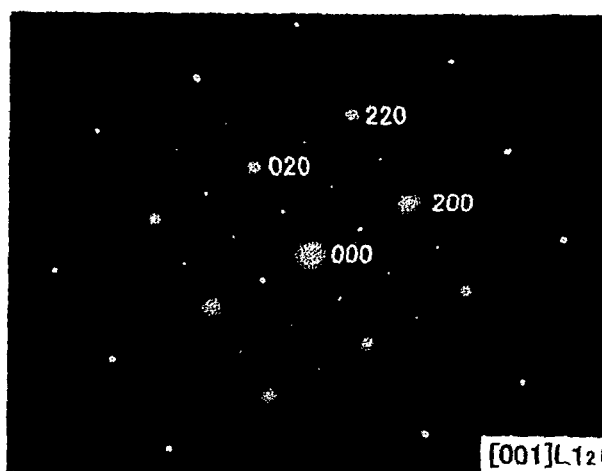
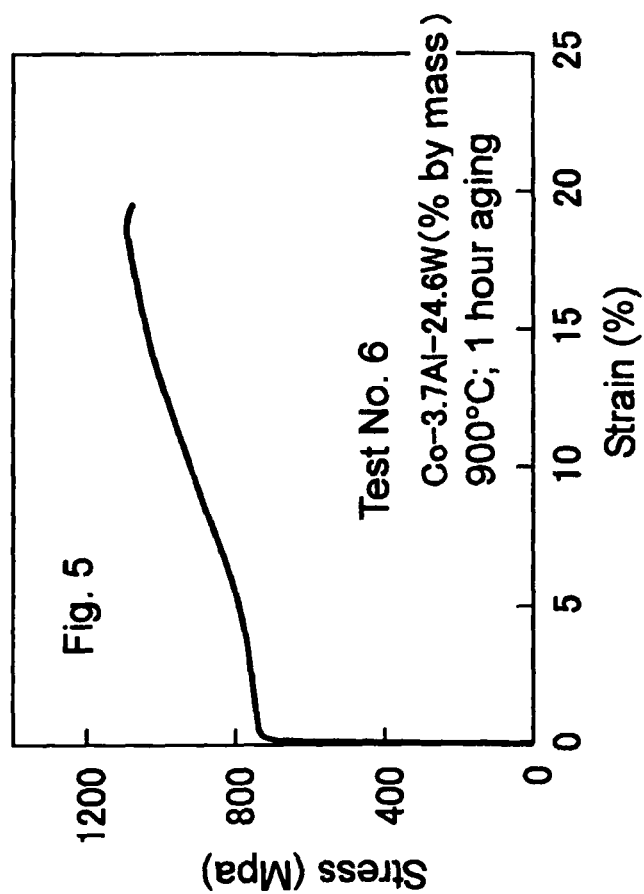
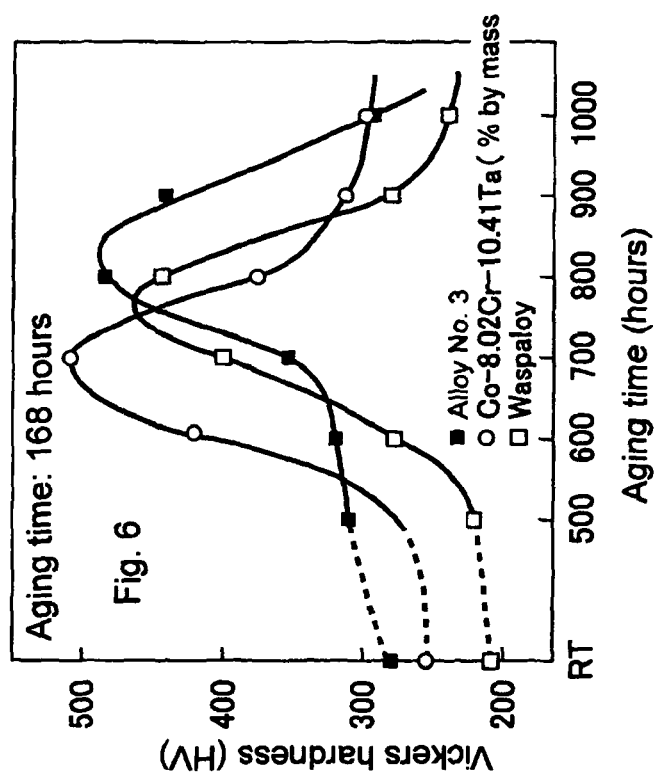
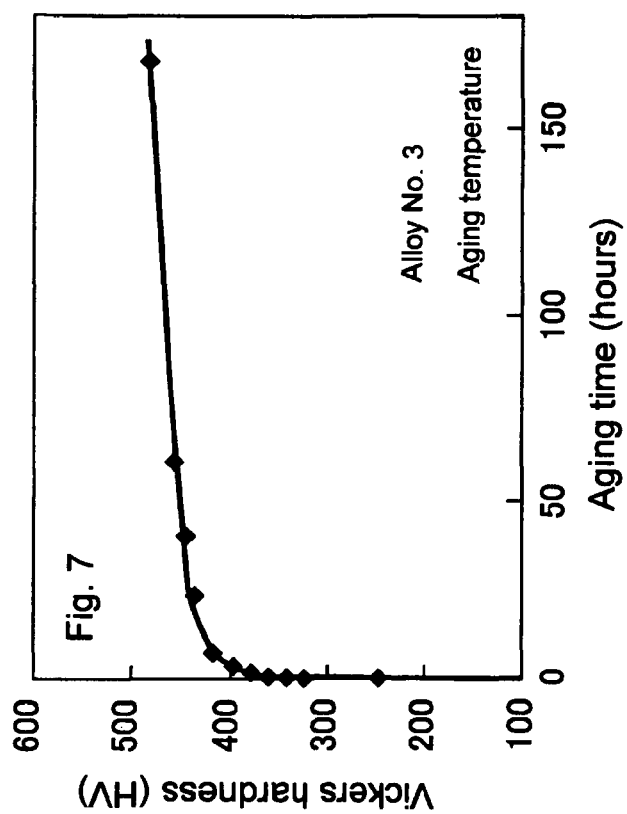


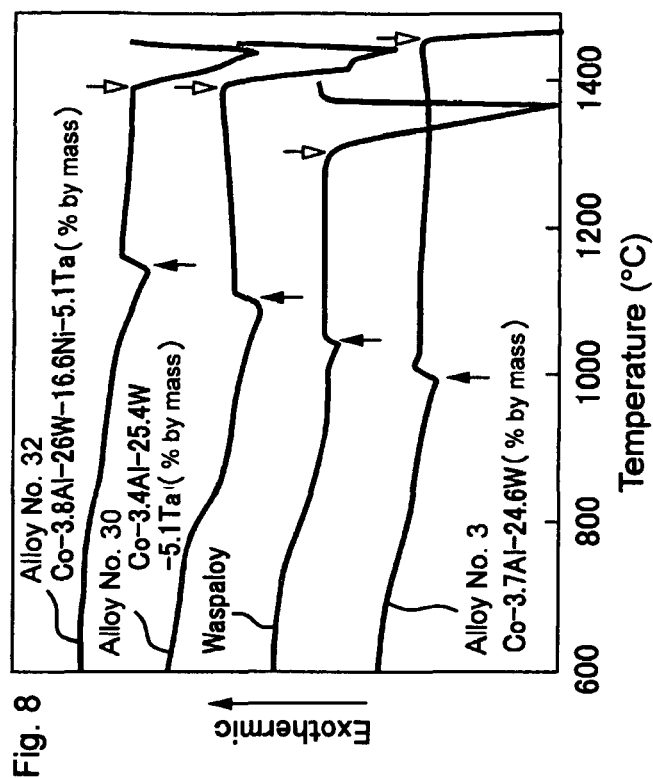
Fig. 4











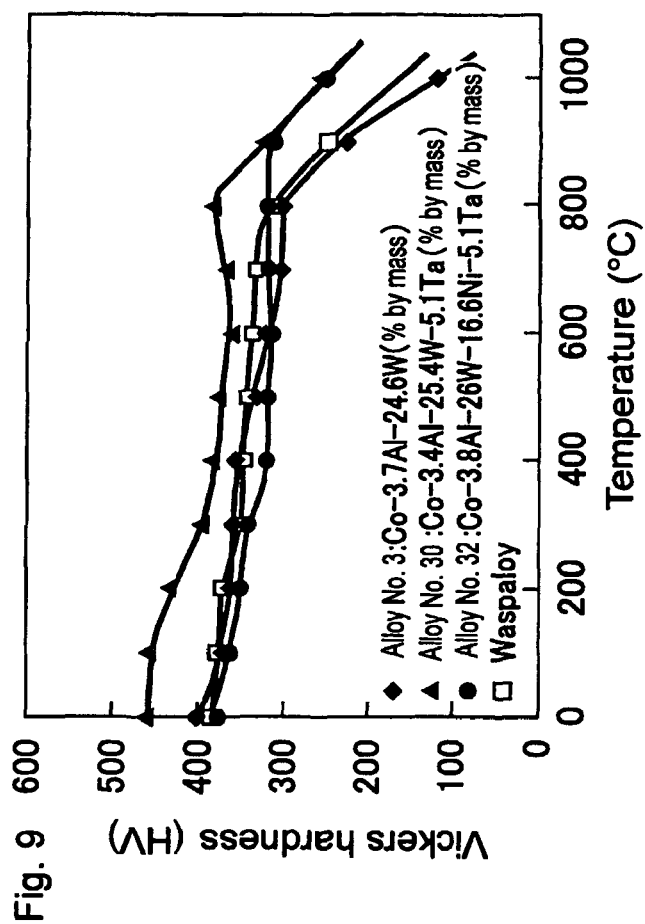


Fig. 10

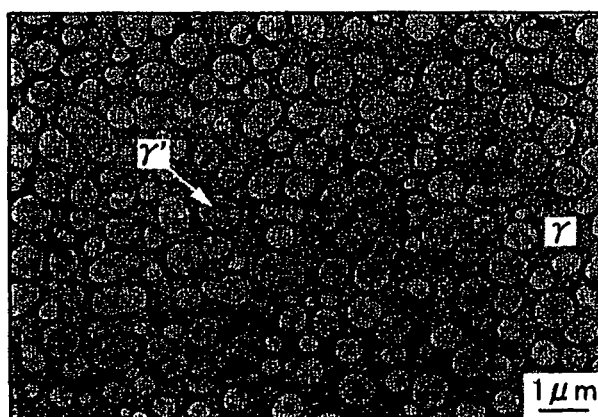
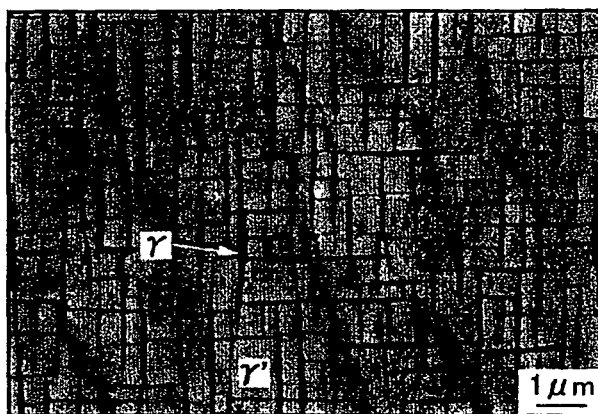
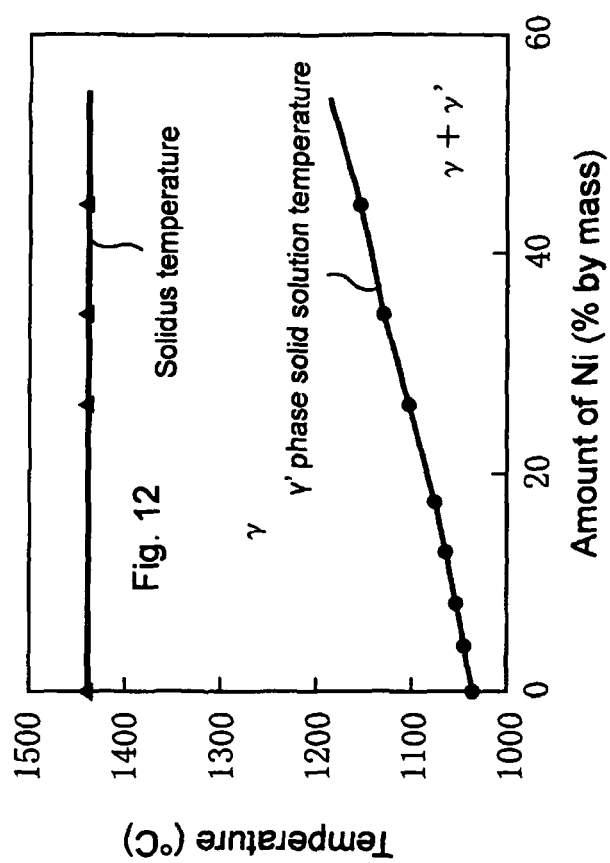


Fig. 11





1

COBALT-BASE ALLOY WITH HIGH HEAT RESISTANCE AND HIGH STRENGTH AND PROCESS FOR PRODUCING THE SAME

This application is a divisional of U.S. application Ser. No. 12/036,880 filed on Feb. 25, 2008, which is a continuation application of PCT/JP2006/317939 filed on Sep. 5, 2006, which is based on and claims the benefit of priority from Japanese Patent Application No. 2005-267964 filed Sep. 15, 2005, which is hereby incorporated by reference.

TECHNICAL FIELD

The present invention relates to a Co-base alloy suitable for applications where a high temperature strength is required or applications where a high strength and a high elasticity are required and process for producing the same.

BACKGROUND ART

With reference to gas turbine members, engine members for aircraft, chemical plant materials, engine members for automobile such as turbocharger rotors, and high temperature furnace materials etc., the strength is needed under a high temperature environment and an excellent oxidation resistance is sometimes required. For that reason, a Ni-base alloy and Co-base alloy have been used for such a high-temperature application. For example, as a typical heat-resistant material such as a turbine blade, a Ni-base superalloy which is strengthened by the formation of γ' phase having an $L1_2$ structure: $Ni_3(Al,Ti)$ is listed. It is preferable that the γ' phase is used to highly strengthen heat-resistant materials because it has an inverse temperature dependence in which the strength becomes higher with rising temperature.

In the high-temperature application where the corrosion resistance and ductility are required, a commonly used alloy is the Co-base alloy rather than the Ni-base alloy. The Co-base alloy is highly strengthened with $M_{23}C_6$ or MC type carbide. Co_3Ti and Co_3Ta etc. which have the same $L1_2$ -type structure as the crystal structure of the γ' phase of the Ni-base alloy have been reported as strengthening phases. However, Co_3Ti has a low melting point and Co_3Ta has a low stability at high temperature. Thus, in the case of using materials made with Co_3Ti and Co_3Ta as strengthening phases, the upper limit of the operating temperature is only about 750° C. even when alloy elements are added. A process including steps of: adding Ni, Al, and Ti etc., precipitating, and strengthening with the γ' phase [$Ni_3(Al,Ti)$] has been reported in Japanese Patent Application Laid-Open (JP-A) No. 59-129746, however, a significant strengthening equal to that of the Ni-base alloy has not been obtained. A process for precipitating and strengthening by using Co_3AlC phase having an $E2_1$ -type intermetallic compound, which has the crystal structure similar to the γ' phase (JP-A No. 10-102175) has also been examined. However, it has not yet been put to practical use.

DISCLOSURE OF THE INVENTION

The present inventors investigated and examined various precipitates which are effective in strengthening the Co-base alloy. As a result, the present inventor discovered a ternary compound $Co_3(Al,W)$ having the $L1_2$ structure and found that the ternary compound was an effective factor in strengthening the cobalt-base alloy. The $Co_3(Al,W)$ has the same crystal structure as a Ni_3Al (γ') phase, which is a major

2

strengthening phase of the Ni-base alloy and has a good compatibility with the matrix. Further, it contributes to the high strengthening of the alloy since it can be precipitated uniformly and finely.

An objective of the present invention is to provide a Co-base alloy with heat resistance equal to that of the conventional Ni-base alloys and an excellent textural stability which is obtained by precipitating and dispersing the $Co_3(Al,W)$ having a high melting point to highly strengthen on the basis of the findings.

The Co-base alloy of the present invention has a basic composition which includes, in terms of mass proportion, 0.1 to 10% of Al, 3.0 to 45% of W, and Co as the substantial remainder and, if necessary, contains one or more alloy components selected from Group (I) and/or Group (II). In this regard, when alloy components of Group (I) are added, the total content is selected from the range of 0.001 to 2.0%.

When alloy components of Group (II) are added, the total content is selected from the range of 0.1 to 50%.

Group (I): 0.001 to 1% of B, 0.001 to 2.0% of C, 0.01 to 1.0% of Y, and 0.01 to 1.0% of La or misch metal
Group (II): 50% or less of Ni, 50% or less of Ir, 10% or less of Fe, 20% or less of Cr, 15% or less of Mo, 10% or less of Re, 10% or less of Ru, 10% or less of Ti, 20% or less of Nb, 10% or less of Zr, 10% or less of V, and 20% or less of Ta, 10% or less of Hf

The Co-base alloy has a two-phase ($\gamma+\gamma'$) texture in which an intermetallic compound of the $L1_2$ -type [$Co_3(Al,W)$] is precipitated on the matrix. In a component system to which an alloy component of Group (II) is added, the $L1_2$ -type intermetallic compound is represented by $(Co,X)_3(Al,W,Z)$. Wherein, X is Ir, Fe, Cr, Re, and/or Ru, Z is Mo, Ti, Nb, Zr, V, Ta, and/or Hf, and nickel is included in both X and Z. Further, a numerical subscript shows atom ratio of each element.

The intermetallic compound [$Co_3(Al,W)$] or [$(Co,X)_3(Al,W,Z)$] is precipitated by performing an aging treatment in the range of 500 to 1100° C. after the solution treatment of the Co-base alloy that is adjusted to a predetermined composition at 1100 to 1400° C. The aging treatment is repeatedly performed at least once or more.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the distribution coefficient of each element in the matrix and γ' phase.

FIG. 2 is a SEM image showing a texture of aging materials of Co-3.6Al-27.3W alloy.

FIG. 3 is a TEM image showing a two-phase texture of aging materials of Co-3.7Al-21.1W alloy.

FIG. 4 is an electron diffraction pattern showing $L1_2$ -type structure of aging materials of Co-3.7Al-21.1W alloy.

FIG. 5 is a graph showing a stress-strain curve of aging materials of Co-3.7Al-24.6W alloy.

FIG. 6 is a graph showing the aging temperature dependence of Vickers hardness.

FIG. 7 is a graph showing the aging time dependence of Vickers hardness.

FIG. 8 is a graph of DSC curves showing phase changes in Co—Al—W ternary alloy, Ta-added Co—Al—W alloy, Co—Ni—Al—W alloy, and Waspaloy.

FIG. 9 is a graph showing the relation between hardness and temperature in Co—Al—W ternary alloy, Ta-added Co—Al—W alloy, Co—Ni—Al—W alloy, and Waspaloy.

FIG. 10 is a SEM image showing a two-phase ($\gamma+\gamma'$) texture of Co—Al—W alloy in which spherical precipitates are formed by adding Mo.

FIG. 11 is a SEM image showing a two-phase ($\gamma+\gamma'$) texture of Co—Al—W alloy in which cubic precipitates are formed by adding Ta.

FIG. 12 is a graph showing an effect of addition of Ni on the transformation temperature of Co—Al—W alloy.

BEST MODE FOR CARRYING OUT THE INVENTION

The Co-base alloy of the present invention has a melting point from about 50 to 100° C., which is higher than that of the Ni-base alloy generally used, and the diffusion coefficient of substitutional element is smaller than Ni-base. Therefore, there is only a slight change in texture when the Co-base alloy is used at high temperature. Further, the deformation processing of the Co-base alloy can be performed by forging, rolling, pressing, and the like since it is rich in ductility as compared with the Ni-base alloy. Thus, it can be expected to put into wide application as compared with the Ni-base alloy.

The mismatch of the lattice constant between the γ' phase of Co_3Ti and Co_3Ta which are conventionally used as strengthening phases and γ matrix is 1% or more, which is disadvantageous from the point of view of creep resistance. On the other hand, the mismatch between the intermetallic compound $[\text{Co}_3(\text{Al},\text{W})]$ which is used as a strengthening phase in the present invention and the matrix is up to about 0.5%, and has a textural stability exceeding that of the Ni-base alloy which is precipitated and strengthened with the γ' phase.

Further, when the intermetallic compound is compared with 200 GPa of the Ni-base alloy, the elastic coefficient is 10% or more (220 to 230 GPa). Thus, the intermetallic compound can be used in applications where the high strength and the high elasticity are required, for example, spiral springs, springs, wires, belts, and cable guides. Since the intermetallic compound is hard and excellent in abrasion resistance and corrosion resistance, it can also be used as a build-up material.

It is preferable that the intermetallic compound of the L1_2 -type $[\text{Co}_3(\text{Al},\text{W})]$ or $[(\text{Co},\text{X})_3(\text{Al},\text{W},\text{Z})]$ is precipitated under conditions where the precipitate's particle diameter is 1 μm or less and volume fraction is about 40 to 85%. When the particle diameter exceeds 1 μm , the mechanical properties such as strength and hardness is easily deteriorated. When the precipitation amount is less than 40%, the strengthening is insufficient. On the other hand, when the precipitation amount exceeds 85%, the ductility tends to be reduced.

In the Co-base alloy of the present invention, the component and composition are specified in order to disperse an appropriate amount of the intermetallic compound of the L1_2 -type $[\text{Co}_2(\text{Al},\text{W})]$ or $[(\text{Co}_3\text{X})_3(\text{Al},\text{W},\text{Z})]$. The Co-base alloy of the present invention has a basic composition which includes, in terms of mass proportion, 0.1 to 10% of Al, 3.0 to 45% of W, and Co as the remainder.

Al is a major constituting element of the γ' phase and contributes to the improvement in oxidation resistance. When the content of Al is less than 0.1%, the γ' phase is not precipitated. Even if it is precipitated, it does not contribute to the high temperature strength. However, the content is set to the range of 0.1 to 10% (preferably 0.5 to 5.0%) because the formation of a brittle and hard phase is facilitated by an excessive amount of Al.

W is a major constituting element of the γ' phase and also has an effect of solid solution strengthening of the matrix. When the content of W is less than 3.0%, the γ' phase is not

precipitated. Even if it is precipitated, it does not contribute to the high temperature strength. When an additive amount of W exceeds 45%, the formation of a harmful phase is facilitated. For that reason, W content is set to the range of 3.0 to 45% (preferably 4.5 to 300).

One or more alloy components selected from Group (I) and Group (II) are added to a basic component system of Co—W—Al, if necessary. In the case where a plurality of alloy components selected from Group (I) are added, the total content is selected from the range of 0.001 to 2.0%. In the case where a plurality of alloy components selected from Group (II) are added, the total content is selected from the range of 0.1 to 50%.

Group (I) is the group consisting of B, C, Y, La, and misch metal.

B is an alloy component which is segregated in the crystal grain boundary to enhance the grain boundary and contributes to the improvement in the high temperature strength. When the content of B is 0.001% or more, the additive effect becomes significant. However, the excessive amount is not preferable in view of the processability, and therefore the upper limit is set to 1% (preferably 0.5%). As with B, C is effective in enhancing the grain boundary. Further, it is precipitated as carbide, thereby improving the high temperature strength. Such an effect is observed when 0.001% or more of C is added. However, the excessive amount is not preferable in view of the processability and toughness, and therefore the upper limit of C is set to 2.0% (preferably 1.0%). Y, La, and misch metal are components effective in improving the oxidation resistance. When the content thereof is 0.01% or more, their additive effects are produced. However, an excessive amount thereof has an adverse effect on the textural stability, and therefore each of the upper limits is set to 1.00 (preferably 0.50).

Group (II) is the group consisting of Ni, Cr, Ti, Fe, V, Nb, Ta, Mo, Zr, Hf, Ir, Re, and Ru. As for alloy components of Group (II), a large distribution coefficient of the element is more effective in stabilizing the γ' phase. The distribution coefficient $K_x^{\gamma/\gamma'}$ is represented by $K_x^{\gamma/\gamma'} = C_x^{\gamma}/C_x^{\gamma'}$ [provided that $C_x^{\gamma'}$: concentration of element x in γ' phase (atomic %), C_x^{γ} : concentration of element x in matrix (γ) phase (atomic %)] and it shows the ratio of concentration of a predetermined element contained in γ' phase to a predetermined element contained in the matrix phase. If the distribution coefficient is 1 or more, it shows a γ' phase stabilized element. If the distribution coefficient is less than 1, it shows the matrix phase stabilized element (FIG. 1). Ti, V, Nb, Ta, and Mo are the γ' phase stabilized elements. Among them, Ta is the most effective element.

Ni and Ir is substituted by Co of the L1_2 -type intermetallic compound and is a component which improves the heat resistance and corrosion resistance. When the content of Ni is 1.0% or more and the content of Ir is 1.0% or more, the additive effects are observed. However, an excessive amount thereof causes the formation of a phase of hazardous compound, and thus the upper limits of Ni and Ir are set to 50% (preferably 40%) and 50% (preferably 40%), respectively. Ni is substituted by Al and W, can improve the stability of the γ' phase, and can maintain the stable state of the γ' phase at higher temperatures.

Fe is also substituted by Co and has an effect of improving processability. When the content of Fe is 1.0% or more, the additive effect becomes significant. However, the excessive amount, more than 10%, is responsible for the instability of texture, and thus the upper limit of Fe is set to 10% (preferably 5.0%).

Cr forms a fine oxide film on the surface of the Co-base alloy and is an alloy component which improves the oxidation resistance. Additionally, it contributes to the improvement in the high temperature strength and corrosion resistance. When the content of Cr is 1.0% or more, such an effect becomes significant. However, the excessive amount causes the processing deterioration, and thus the upper limit of Cr is set to 20% (preferably 15%).

Mo is an effective alloy component for the stabilization of the γ' phase and solid solution strengthening of the matrix. When the content of Mo is 1.0% or more, the additive effect is observed. However, the excessive amount causes the processing deterioration, and thus the upper limit of Mo is set to 15% (preferably 10%).

Re and Ru are components effective in improving the oxidation resistance. When the content thereof is 0.5% or more, the additive effects become significant. However, an excessive amount thereof causes inducing the formation of a harmful phase, and thus the upper limits of Re and Ru are set to 10% (preferably 5.0%).

Ti, Nb, Zr, V, Ta, and Hf are effective alloy components for the stabilization of the γ' phase and the improvement in the high temperature strength. When the content of Ti is 0.5% or more, the content of Nb is 1.0% or more, the content of Zr is 1.0% or more, the content of V is 0.5% or more, the content of Ta is 1.0% or more, and the content of Hf is 1.0% or more, the additive effects are observed. However, an excessive amount thereof causes the formation of harmful phases and the melting point depression, and thus the upper limits of Ti, Nb, Zr, V, Ta, and Hf are set to 10%, 20%, 10%, 10%, 20%, and 10%, respectively.

In the case where the Co-base alloy, which is adjusted to a predetermined composition, is used as a casting material, it is produced by any method such as usual casting, unidirectional coagulation, squeeze casting, and single crystal method. It can be hot-worked at a solution treatment temperature and has a relatively good cold-working property. Therefore it can also be processed into a plate, bar, wire rod, and the like.

The Co-base alloy is formed into a predetermined shape and then heated in the solution treatment temperature range of 1100 to 1400° C. (preferably 1150 to 1300° C.). The strain introduced by processing is removed and the precipitate is solid-solutioned in the matrix in order to homogenize the material. When the heating temperature is below 1100° C., neither the removal of strain nor the solid solution of precipitate proceeds. Even if both of them proceed, it takes a lot of time, which is not productive. On the other hand, when the heating temperature exceeds 1400° C., some liquid phase is formed and the roughness of the crystal grain boundary and the coarsening growth of the crystal grains are facilitated, which results in reducing the mechanical strength.

The Co-base alloy is subjected to solution treatment, followed by aging treatment. In the aging treatment, the Co-base alloy is heated in the temperature range of 500 to 1100° C. (preferably 600 to 1000° C.) to precipitate $\text{Co}_3(\text{Al,W})$. $\text{Co}_3(\text{Al,W})$ is the L1_2 -type intermetallic compound and the lattice constant mismatch between $\text{Co}_3(\text{Al,W})$ and the matrix is small. It is excellent in the high temperature stability as compared to the γ' phase $[\text{Ni}_3(\text{Al,Ti})]$ of the Ni-base alloy and contributes to the improvement in the high temperature strength and heat resistance of the cobalt-base alloy. $(\text{Co,X})_3(\text{Al,W,Z})$ in the component system to which an alloy component of Group (II) is added contributes to the improvement in the high temperature strength and heat resistance of the cobalt-base alloy.

As for a γ' phase with a L1_2 structure which is used as a strengthening phase, γ' Ni_3Al phase is a stable phase in an equilibrium diagram of Ni—Al binary system. Thus, in the Ni-base alloy using this system as a basic system, the γ' phase has been used as a strengthening phase. In an equilibrium diagram of Co—Al system, Co_3Al phase is not present and it is reported that the γ' phase is a metastable phase. It is necessary to stabilize the metastable γ' phase in order to use the γ' phase as a strengthening phase of the Co-base alloy. In the present invention, the stabilization of the metastable γ' phase is achieved by adding W. It is considered that γ' L1_2 phase (composition ratio: $\text{Co}_3(\text{Al,W})$ or $(\text{Co,X})_3(\text{Al,W,Z})$) is precipitated as a stable phase.

It is preferable that the intermetallic compound $[\text{Co}_3(\text{Al,W})]$ or $[(\text{Co,X})_3(\text{Al,W,Z})]$ is precipitated on the matrix under conditions where the particle diameter is 50 nm to 1 μm and the precipitation amount is about 40 to 85% by volume. Precipitation-strengthening effect is obtained when the particle diameter of the precipitate is 10 nm or more. However, the precipitation-strengthening effect is reduced when the particle diameter exceeds 1 μm . For the purpose of obtaining sufficient precipitation-strengthening effect, it is required that the precipitation amount is 40% by volume or more. However, when the precipitation amount exceeds 85% by volume, the ductility tends to be lowered. In order to give a preferable particle diameter and precipitation amount, it is preferable that the aging treatment is performed gradually in a predetermined temperature region.

As for the prices of metal materials themselves, Co is more expensive than Ni. In many cases, the manufacturing/processing cost accounts for a large percentage of the actual price. For example, in the case of the Ni-base alloy turbine blade, the material cost is estimated about 5% of the total cost. Even if the expensive Co is used, the extra material cost is only several percent of the total cost. Taking into consideration advantages of the increase in the working temperature of a heat engine and a longer operating life, it is considered that the Co is sufficient for practical use. Therefore, taking advantage of an excellent high temperature characteristic, it contemplated that the member conventionally made with the Co-base heat-resistant alloy is highly strengthened and an alternate application where the member made with the Ni-base alloy is used is also expected. Specifically, it can be used as a suitable material for gas turbine members, engine members for aircraft, chemical plant materials, engine members for automobile such as turbocharger rotors, and high temperature furnace materials etc. Since it has the high strength as well as the high elasticity and is excellent in corrosion resistance, it can be used as a material for build-up materials, spiral springs, springs, wires, belts, cable guides, and the like.

Example 1

The Co-base alloy with the composition of Table 1 was smelted by high-frequency-induction dissolution in an inert gas atmosphere. The resulting product was casted to form an ingot, and then hot-rolled to a plate thickness of 3 mm at 1200° C. The test pieces obtained from the ingot and the hot-rolled plate were subjected to the solution treatment and aging treatment shown in Table 2, followed by texture observation, composition analysis, and characteristic test.

Each of the test results is shown in Table 3. In the Table, $\gamma'/\text{D0}_{19}$ shows that precipitates are two types of γ' phase and D0_{19} (Co_3W) phase, $\text{D0}_{19}/\mu$ shows that precipitates are two types of D0_{19} phase and μ phase, and $\text{B2}/\mu$ shows that precipitates are two types of B2 (CoAl) phase and μ phase.

7

In the samples of Test Nos. 1 to 13, one type of the γ' phase was observed as a precipitate. As is apparent from the case of Test Nos. 1 and 2, it is found that a mechanical property such as hardness can be controlled by changing the precipitation amount of the γ' phase in the aging treatment even if the alloy has the same composition. When the γ' amount is extremely increased, the ductility at room temperature tends to be lowered (Test Nos. 9 to 12). Vickers hardness at 800° C. is as sufficiently-high as about 300 and good high temperature characteristics are obtained. Alloy No. 3 is an alloy design that values compatibility between the strength and the ductility. In Examples 2 and 3 described below, Alloy No. 3 is used as a basic composition.

In Test Nos. 14 to 19, the precipitates of D0₁₉ phase and B2 phase etc. were detected in addition to the γ' phase. The precipitates of D0₁₉ phase and B2 phase etc. were preferentially precipitated in the crystal grain boundary and the γ' phase was precipitated in the grain. The high hardness of the grains was maintained up to an elevated temperature due to the precipitation form in the grain boundary and the grains. However, the elongation at break at room temperature was reduced.

The Co-base alloys in Test Nos. 13 and 14 had the same composition. However, D0₁₉ phase was not precipitated in the case of Test No. 13 because of a short time heat treatment and a relatively large elongation was observed. Thus, only γ' phase can be precipitated by a short-time aging treatment and it can be applied to members to be used at a relatively low temperature.

Test Nos. 20 and 21 show the characteristics of Alloy Nos. 12 and 13 (comparative materials). In these alloys, the γ' phase was not precipitated. The precipitation of a very weak μ phase resulted in the hardness, while the ductility was extremely poor.

8

TABLE 1

Classification	Smelted cobalt-base alloy (Co; impurities removed from the remainder)		
	Alloy component (% by mass)		
	Alloy No.	Al	W
Example of the present invention	1	3.7	21.1
	2	3.5	26.8
	3	3.7	24.6
	4	3.6	27.3
	5	3.5	30.0
	6	1.9	26.3
	7	0.5	40.9
	8	1.5	30.3
	9	2.8	31.9
	10	4.4	14.8
Comparative example	11	7.5	5.0
	12	3.1	52.8
	13	13.1	29.7

TABLE 2

Heat treatment conditions				
Heat treatment No.	Solution treatment		Aging treatment	
	(° C.)	(Time)	(° C.)	(Time)
1	1300	2	100	168
2	1300	2	900	138
3	1300	2	900	1
4	1300	2	900	168
5	1300	2	900	96
6	1400	1	900	1
7	1400	1	800	96

TABLE 3

Alloy components, metal compositions in accordance with heat treatment conditions, and physical properties										
Test No.	Alloy No.	Heat treatment No.	Precipitated intermetallic compound Type	Strength			Elongation at break (%)	Vickers hardness		Oxidation resistance
				Precipitation amount (volume %)	(MPa)	(MPa)		(25° C.)	(800° C.)	
1	1	4	γ'	49	1310	975	23	467	290	Δ
2	1	2	γ'	30	1044	668	25	327	225	Δ
3	2	4	γ'	75	1335	951	12	484	331	\bigcirc
4	3	1	γ'	10	758	542	25	268	226	Δ
5	3	2	γ'	50	1214	834	17	422	309	\bigcirc
6	3	3	γ'	65	1085	737	21	385	—	\bigcirc
7	3	4	γ'	65	1345	995	11	481	310	\bigcirc
8	3	5	γ'	65	1320	971	14	473	308	\bigcirc
9	4	6	γ'	75	660	650	0.5	360	—	\bigcirc
10	4	7	γ'	75	702	671	4	457	292	\bigcirc
11	5	6	γ'	80	590	520	4	336	—	Δ
12	5	7	γ'	80	674	629	3	426	324	Δ
13	6	3	γ'	40	940	676	16	305	—	Δ
14	6	4	γ' /D0 ₁₉	70	1197	922	8	450	305	Δ
15	7	4	γ' /D0 ₁₉	55	935	822	6	525	335	Δ
16	8	4	γ' /D0 ₁₉	65	1026	862	8	483	301	Δ
17	9	4	γ' /D0 ₁₉	85	765	716	4	432	278	\bigcirc
18	10	4	γ' /B2	25	658	619	4	305	197	\bigcirc
19	11	4	γ' /B2	10	652	631	2	412	220	\bigcirc
20	12	2	D0 ₁₉ / μ	—	421	—	<0.1	478	—	X
21	13	2	B2/ μ	—	220	—	<0.1	671	—	\bigcirc

9

FIG. 2 is a SEM image of Alloy No. 4 which was subjected to aging treatment at 1000° C. for 168 hours. As shown in FIG. 2, fine precipitates having the cubic shape were uniformly dispersed and had the same texture as the Ni-base superalloy conventionally used. As also shown in a TEM image of Alloy No. 1 which was subjected to aging treatment at 900° C. for 72 hours (FIG. 3), fine precipitates having the cubic shape were uniformly dispersed. From an electronic diffraction image (FIG. 4), they were identified as precipitates with the L1₂-type crystal structure.

The precipitates that were precipitated by aging treatment had a characteristic unlikely to be coarsened. Even after heat treatment at 800° C. for 600 hours, an average particle diameter was 150 nm or less. The characteristic unlikely to be coarsened indicated that the stability of texture was good. Such a uniform precipitation of the L1₂ phase was not detected in Comparative examples.

As shown in the stress-strain curve (FIG. 5), the mechanical properties of Alloy No. 3 are as follows: tensile strength: 1085 MPa, 0.2% proof strength: 737 MPa, and elongation at break: 21%. The mechanical properties were the same as that of the Ni-base alloy such as Waspaloy or more than that. However, when the γ' phase fraction becomes large, the ductility tends to be lowered. Thus, it is preferable to adjust the γ' phase fraction to the range of 40 to 85% by volume.

As is apparent from the aging time dependence of Vickers hardness (FIG. 6) as well as the aging time dependence of Vickers hardness (FIG. 7), the increase of hardness by aging for 168 hours was significant at 700 to 900° C. in the case of Alloy No. 3. In the case of the heating temperature exceeding 900° C., the precipitates are coarsened. On the other hand, in the case of the heating temperature less than 600° C., the precipitates are insufficient. It is surmised that both cases cause for preventing the alloy from being hard-

10

TABLE 4

Smelted cobalt-base alloy (Co; impurities removed from the remainder)						
Alloy component and content (% by mass)						
Alloy No.	Al	W	B	C	Y	La
14	3.7	25.0	0.2	—	—	—
15	3.7	25.0	—	0.7	—	—
16	3.7	25.0	—	—	0.4	—
17	3.7	25.0	—	—	—	0.4
18	3.7	25.0	0.03	0.03	—	—

Since all components other than C were added trace elements in Group (I), a major change in the texture other than the addition of C was not observed. When a carbide is precipitated by addition of C, the Co-base alloy becomes hard. Both C and B tend to be segregated in the grain boundary segregation and they contribute to the improvement in high temperature creep strength. When the mechanical properties at room temperature was observed, 0.2% proof strength was increased as compared to Alloy No. 3 (ternary alloy). However, the elongation at break was reduced and the tensile strength showed an approximate equivalent value. It is known that the addition of Y and La is effective in improving the oxidation resistance of the Ni-base alloy. The same effect is also observed in the component system of the present invention. In addition, the elements of Group (I) does not have a substantial adverse influence on the stability and mechanical properties of the γ' phase, and therefore it can be expected as a very effective additive component.

TABLE 5

Alloy components, metal compositions in accordance with heat treatment conditions, and physical properties										
Heat treatment			Precipitated intermetallic compound		strength	strength	Elongation	Vickers		Oxidation
Test No.	Alloy No.	No.	Precipitation amount	(volume %)	(MPa)	(MPa)	at break	hardness		resistance
			Type		(MPa)	(MPa)	(%)	(25° C.)	(800° C.)	
22	14	4	γ'	60	1366	1018	10	487	282	○
23	15	4	γ' /Carbide	45	1228	1095	8	625	346	○
24	16	4	γ'	60	1310	918	15	445	280	⊗
25	17	4	γ'	60	1339	934	15	461	277	⊗
26	18	4	γ'	60	1244	1035	7	488	296	○

ened. In addition, the hardness of Co—Cr—Ta alloy and Waspaloy are also shown in FIG. 6 for comparison. A peak of hardness as to Alloy No. 3 was observed at higher temperatures as compared to the others. The increase of hardness, in other words, the precipitation of the γ' phase, proceeded very rapidly up to about 5 hours. As is found in FIG. 7, the increase proceeded gradually after 5 hours.

Example 2

Table 4 shows alloy designs in which alloy components of Group (I) were added to Co—W—Al alloy. The amounts of Al and W were determined based on Alloy No. 3 of Table 1. The cobalt-base alloy adjusted to a predetermined composition was dissolved, casted, and hot-rolled in the same manner as described in Example 1, followed by heat-treating. The characteristics of the obtained hot-rolled plates are shown in Table 5.

Example 3

Table 6 shows alloy designs in which alloy components of Group (II) were added to Co—W—Al alloy. The Co-base alloy adjusted to a predetermined composition was dissolved, casted, and hot-rolled in the same manner as described in Example 1, followed by heat-treating. The characteristics of the obtained hot-rolled plates are shown in Table 7. For comparison, physical properties of Ni-base superalloy Waspaloy (Cr: 19.5%, Mo: 4.3%, Co: 13.5%, Al: 1.4%, Ti: 3%, C: 0.07%) are shown in Table 7 as Alloy No. 33.

TABLE 6

Smelted cobalt-base alloy (Co; impurities removed from the remainder)			
Alloy component and content (% by mass)			
Alloy No.	Al	W	Alloy component of Group (II)
19	4.0	26.9	Ni: 4.3
20	3.4	25.4	Ir: 5.4
21	3.5	26.4	Fe: 1.6
22	3.5	26.4	Cr: 1.5
23	3.4	26.1	Mo: 2.8
24	3.4	25.4	Re: 5.3
25	3.5	26.4	Ti: 1.4
26	3.4	26.1	Zr: 2.6
27	3.4	25.5	Hf: 5.0
28	3.5	26.4	V: 1.5
29	3.4	26.1	Nb: 2.7
30	3.4	25.4	Ta: 5.1
31	3.6	23.9	Cr: 3.7, Ta: 5.2
32	3.8	26.0	Ni: 16.6, Ta: 5.1

TABLE 7

Alloy components, metal compositions in accordance with heat treatment conditions, and physical properties										
Test	Alloy	Heat treatment	Precipitated intermetallic compound		strength (MPa)	strength (MPa)	Elongation at break (%)	Vickers hardness		Oxidation resistance
			Precipitation amount (volume %)	Type				(25° C.)	(800° C.)	
27	19	4	65	γ'	13.7	874	24	460	320	○
28	20	4	60	γ'	1395	920	18	510	345	⊗
29	21	4	45	$\gamma'/B2$	1180	772	12	406	287	○
30	22	4	35	$\gamma'/D0_{19}$	1136	790	16	411	290	⊗
31	23	4	40	$\gamma'/D0_{19}$	1319	836	16	452	311	○
32	24	4	60	γ'	1402	870	20	455	310	⊗
33	25	4	70	γ'	1221	756	24	442	309	Δ
34	26	4	75	$\gamma'/D0_{19}$	1252	813	12	421	280	Δ
35	27	4	75	$\gamma'/D0_{19}$	1240	922	9	488	338	○
36	28	4	70	γ'	1203	790	18	415	383	Δ
37	29	4	70	$\gamma'/D0_{19}$	1186	804	13	421	310	○
38	30	4	75	$\gamma'/D0_{19}$	1365	955	14	531	390	○
39	31	4	65	$\gamma'/D0_{19}$	1371	952	15	503	307	⊗
40	32	4	70	γ'	1410	920	20	385	335	⊗
41	33	—	48	γ'	1275	795	25	410	309	⊗

DSC curves of Alloy No. 3, Alloy No. 30, Alloy No. 32, and Alloy No. 33 (Waspaloy) are shown in FIG. 8. As for Alloy No. 30, the γ' solid solution temperature indicated by black arrows was highly increased as compared to that of the ternary alloy to which Ta was added. It is found that the γ' phase was stably present up to a temperature higher than that of Waspaloy. It can be understood that Alloy Nos. 3 and 30 are more excellent in heat resistance in comparison with that of Alloy No. 33 from the fact that the solidus temperature indicated by white arrows (temperature where a liquid phase is formed) is high. Alloy No. 32 is an alloy that a part of Co in Alloy No. 30 is substituted by Ni. The γ' solid solution temperature was further increased and the solidus temperature was hardly reduced.

The results of measurement of the high temperature hardness of alloy Nos. 3, 30, 32, and 33 are shown in FIG. 9. Alloy No. 3 had the same hardness as that of Alloy No. 33, while Alloy No. 30 to which Ta was added showed hardness higher than that of Alloy No. 33 in the temperature range of room temperature to 1000° C. Its mechanical properties were superior to the conventional Ni-base alloy. As a result, it can be said that it is a very promising heat-resistant material. Alloy No. 32 had the nearly same hardness as that of Alloy No. 3 (ternary alloy) at room

temperature immediately after the aging treatment. The γ' phase was stable up to an elevated temperature, and thus the hardness was hardly decreased at high temperature and a value comparable to that of Alloy No. 30 was observed at 1000° C.

Two-phase ($\gamma+\gamma'$) textures of Alloy No. 23 and Alloy No. 30, which were subjected to aging treatment at 1000° C. for 168 hours, was shown in FIGS. 10 and 11, respectively. In Alloy No. 23 to which Mo was added, the γ' phase was spheroidized. In Alloy No. 30 to which Ta was added, the γ' phase having the cubic shape was precipitated. The difference in the precipitation form derives from the difference in lattice constant (lattice mismatch) between the matrix (γ phase) and the γ' phase and it has also a large effect on the high temperature characteristics of the materials. In the present component system, the precipitation form can be changed by a very small amount of additive elements. Thus, various alloy designs according to applications and the texture control can be achieved.

In Group (II), Fe and Cr which are matrix (γ) stabilized elements cause the reduction of precipitation amount of the γ' phase and the decrease of the solid solution temperature. Since Cr has a significant effect on the improvement of the oxidation resistance and the corrosion resistance, it can be said that it is an essential element from a practical standpoint. In the aging treatment, the precipitation of a brittle and hard B2 (CoAl) phase is facilitated by Fe, which causes the decrease in the ductility. When Fe is in the solution-treated state, it conversely contributes to the improvement in the processability. Thus, the additive amount is adjusted in accordance with the intended use.

The distribution coefficient of Ni is nearly 1 and an equivalent amount of Ni is distributed on the matrix and the precipitates. However, the research results by the present inventors indicate that the solid solution temperature of the γ' phase rises with increased amounts of Ni while the solidus temperature hardly decreases, as shown in the solid solution temperature and the solidus temperature of the γ' phase of Co-4Al-26.9W ternary system alloy to which various amounts of Ni were added (FIG. 12). This corresponds to the result of Alloy No. 32 whose hardness is gradually decreased at high temperature by adding Ni and which has an excellent high temperature characteristic.

13

With reference to Alloy No. 20 to which Ir was added, the hardness and tensile strength at room temperature were increased in addition to the oxidation resistance. The oxidation resistance of Alloy No. 24 was improved by adding Re, while the obtained mechanical properties were not as effective as that of Ir.

All elements of Groups 4 and 5 such as Ti, Zr, Hf, V, and Nb stabilize the γ' phase and increase the precipitation amount, and therefore they impart a good characteristic to the phase at both room temperature and high temperature. However, they have a role in facilitating the precipitation of DO_{19} (Co_3W) phase. Although the DO_{19} phase does not have adverse influence on the ductility like the B2 phase, it is easily coarsened as compared to the γ' phase. Thus, it is necessary to control the additive amount in an actual alloy design.

Alloy Nos. 31 and 32 are cobalt-base alloys with combined addition of Cr and Ta and combined addition of Ni and Ta, respectively. Both alloys were excellent in the oxidation resistance and had a high temperature hardness equal to that of Waspaloy alloy as well as a sufficient ductility.

The invention claimed is:

1. A process for producing a cobalt-base alloy with high heat resistance and high strength, the cobalt-base alloy comprising a composition of, in terms of mass proportion: 0.1 to 10% of Al, 3.0 to 45% of W both amounting to less than 50% in total content and Co as a remainder containing indispensable impurities, the process comprising the steps of:

solution-treating the Co base-alloy with the composition in a temperature range of 1100 to 1400° C. for one to two hours after forming the Co base-alloy into a predetermined shape; and

subsequently performing aging treatment on the solution-treated Co base-alloy in a temperature range of 500 to 1100° C. for one to 168 hours so as to form

a matrix phase (γ phase) essentially consisting of Co having an fcc structure and

a precipitation phase (γ' phase) comprising a $L1_2$ -type intermetallic compound of $Co_3(Al,W)$ by atom ratio having an fcc structure, and

wherein the precipitation phase (γ' phase) is precipitated in particles of the matrix phase, and

a particle diameter of the precipitation phase (γ' phase) of $Co_3(Al,W)$ ranges from 50 nm to 1 μ m and a precipitation amount thereof ranges from 40 to 85% by volume fraction, and

a lattice mismatch between the matrix phase (γ phase) of the cobalt-base alloy and the precipitation phase (γ' phase) of $Co_3(Al,W)$ thereof is 0.5% or less.

2. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 1, wherein a Vickers hardness of the cobalt-base alloy at 800° C. is 250 or higher.

3. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 1, wherein the cobalt-base alloy includes a DO_{19} type intermetallic compound of Co_3W by atom ratio to be precipitated in the matrix phase (γ phase).

4. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 1, wherein the cobalt-base alloy includes a B2 phase intermetallic compound of CoAl by atomic ratio to be precipitated in the matrix phase (γ phase).

5. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 1,

14

wherein the cobalt-base alloy comprises one or more components selected from the following Group (I) in a total of 0.001 to 2.0% by mass, the Group (I) being defined as: 0.001 to 1.0% of B, 0.001 to 2.0% of C, 0.01 to 1.0% of Y, and 0.01 to 1.0% of La or misch metal.

6. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 5, wherein a Vickers hardness of the cobalt-base alloy at 800° C. is 250 or higher.

7. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 5, wherein the cobalt-base alloy includes a DO_{19} type intermetallic compound of Co_3W by atom ratio to be precipitated in the matrix phase (γ phase).

8. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 5, wherein the cobalt-base alloy includes a B2 phase intermetallic compound of CoAl by atomic ratio to be precipitated in the matrix phase (γ phase).

9. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 5, wherein the cobalt-base alloy to which the C component is added includes carbide to be precipitated in the matrix phase (γ phase).

10. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 1, wherein the cobalt-base alloy further comprises one or more components selected from the following Group (II) in a total of 0.1 to 50% by mass,

wherein a $L1_2$ -type intermetallic compound precipitated is $(Co, X)_3(Al,W, Z)$ by atom ratio, and the Group (II) being defined as: X being Ir, Fe, Cr, Re, and/or Ru; Z being Mo, Ti, Nb, Zr, V, Ta, and/or Hf; and nickel being comprised in both X and Z.

11. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 10, wherein a Vickers hardness of the cobalt-base alloy at 800° C. is 250 or higher.

12. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 10, wherein the cobalt-base alloy includes a DO_{19} type intermetallic compound of Co_3W by atom ratio to be precipitated in the matrix phase (γ phase).

13. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 10, wherein the cobalt-base alloy includes a B2 phase intermetallic compound of CoAl by atomic ratio to be precipitated in the matrix phase (γ phase).

14. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 5, wherein the cobalt-base alloy further comprises one or more components selected from the following Group (II) in a total of 0.1 to 50% by mass, wherein a type $L1_2$ -type intermetallic compound precipitated is $(Co, X)_3(Al,W, Z)$ by atom ratio, and the Group (II) being defined as: X being Ir, Fe, Cr, Re, and/or Ru; Z being Mo, Ti, Nb, Zr, V, Ta, and/or Hf; and nickel being comprised in both X and Z.

15. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 14, wherein a Vickers hardness of the cobalt-base alloy at 800° C. is 250 or higher.

16. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim 14, wherein the cobalt-base alloy includes a DO_{19} type intermetallic compound of Co_3W by atom ratio to be precipitated in the matrix phase (γ phase).

15

17. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim **14**, wherein the cobalt-base alloy includes a B2 phase inter-metallic compound of CoAl by atomic ratio to be precipitated in the matrix phase (γ phase).

5

18. The process for producing a cobalt-base alloy with high heat resistance and high strength according to claim **14**, wherein the cobalt-base alloy to which the C component is added includes carbide to be precipitated in the matrix phase (γ phase).

10

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16